

The Positive Ions from Hot Metals.

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It is well known that when a metal wire or strip is heated for the first time there is a large emission of positive ions from it at a comparatively low temperature. This emission takes place even if the wire is carefully cleaned and the heating is carried out in a good vacuum. It decays to a small value under continuous heating in a vacuum, and can be revived to a varying extent by a number of different modes of treatment, such as heating in air, or in a bunsen flame, or by subjection to high pressure. Very different conclusions as to the nature of these ions have been reached by different experimenters. One view, which has, perhaps, had more advocates than any other, is that the ions consist of positively charged atoms or molecules of various gases evolved by the hot substances. For several years I have suspected that these ions would turn out to be atoms or molecules of the commoner alkali metals which are present in the heated metals as impurities. The experiments to be described were undertaken in the hope of deciding the question in a definite manner.

The direct and obvious way of attacking the problem is to determine the specific charge (e/m) of the carriers. Since the value of the corresponding quantity for the standard chemical element in electrolysis is known, this is equivalent to measuring the electric atomic (or equivalent) weight (m/H). I have already made experiments with a large number of metallic substances in this way, partly in collaboration with Mr. Hulbirt.* The results showed that the electric atomic weight of the ions was of the order of 30 for the 14 different substances tested, but the measurements were not sufficiently exact to determine with certainty whether the ions were atoms of sodium and potassium or molecules of some of the commoner gases, such as carbon monoxide. The electric equivalent weight of CO_+ is 28, and is thus intermediate between Na_+ (23.05) and K_+ (39.1). There are a number of other alternative constituents which suggest themselves.

The method of measurement was the same in principle as that used in the earlier experiments, but has been improved in a number of details, so as to ensure higher accuracy. The entire apparatus has been enlarged, so that the distance between the slit and the strip ranged around 1.35 cm. instead of

* 'Phil. Mag.,' 1908, vol. 16, p. 740; 1910, vol. 20, p. 545.

0.45 cm., the other dimensions being made to correspond. The strips were cut 0.1 cm. wide with the dividing engine, and almost filled the slit in the brass plate in which they were placed, only about 0.01 cm. clearance being left on either side. As the formula for e/m contains the distance between the strip and the opposite slit raised to the fourth power, it is important that this distance should be perfectly definite and capable of precise measurement. An improved method of measuring this distance was employed. A low-power reading microscope, with its axis horizontal, was arranged to travel in a vertical direction. The axis of the microscope pointed lengthwise along the middle line of the strip and of the slit, which was vertically above the strip. The microscope was focussed on the point of a pin placed at the centre of the strip before measuring the distance between strip and slit. Thus the distance measured was that at the middle, but measurements made in other parts did not show any appreciable difference.

The greatest source of uncertainty in the earlier measurements, in all probability, is caused by the bowing of the heated strip due to thermal expansion. The change in the distance between the strip and the opposite slit which is produced in this way is rather variable, as it depends on the stiffness of the strip and the way in which it is attached to the end supports. It may, however, introduce quite serious errors into the final value of e/m . This difficulty was entirely overcome in the present experiments by mounting one of the platinum terminals, to which one of the ends of the strip was attached, on the free end of a strip of phosphor bronze several centimetres long and of suitable thickness. The heated metal strip was then at right angles to the phosphor bronze strip, which was arranged to keep it under a slight tension. The extent of the outward motion of the phosphor bronze spring was limited, and could be regulated, by a small screw. A good deal of difficulty was experienced at first in getting the amount of tension right. If the spring is too stiff it breaks the metal strip, which becomes quite soft at a high temperature; on the other hand, if it is too weak, it is not able to keep the heated strip taut. After some trials it was found that the proper amount of tension could be estimated without much difficulty.

The strip itself was soldered to platinum studs, one of which was attached to the phosphor bronze spring in the manner just described. The ends of the studs were the least bit below the surface of the plate, and the strip was pulled over them and bent round, and then soldered to the side of the studs. The tension of the spring caused a good electrical contact to be established between the strip and the ends of the studs, where there was no solder. In this way there was no danger of the solder getting on to the hot parts of the

strip. The strips were accurately cut in the dividing engine, so as to be uniform in width, and were very carefully cleaned. In the case of platinum they were boiled in hydrofluoric acid, nitric acid, and distilled water in succession. When mounted they were flush with the brass plate. Both this plate and the opposite divided plate were ground flat and mounted so as to be parallel. The hard rubber blocks, to which the plates were formerly screwed, were discarded, and replaced by quartz tubes, accurately ground perpendicular to their axes, so as to be equal in length. The plates were held together by brass screws, which passed through holes in the plates and down the centre of the quartz tubes. The screws and nuts were insulated from the brass plates by hard rubber bushings. In this way changes in the distance, which might have been caused by the somewhat considerable and rather irregular expansion of the hard rubber, were eliminated. The micrometer screw which was used for measuring the displacement of the maxima was carefully checked up. It was found that the errors were too small to be worthy of consideration.

Many other changes have been made in the mechanical construction of this apparatus since the form figured in the 'Philosophical Magazine,' 1908, vol. 16, pp. 744, 747, was made. The construction of the tube has been altered, so that the plates lie in horizontal instead of vertical planes. There are now three leads corresponding to A and B (fig. 2, *loc. cit.*), one for the electrode behind the slit and the others for the two plates. Thus, either the slit or balance method* may be employed by simply changing the connections outside the tube. These leads are provided with brass springs, and are connected to the apparatus with platinum hooks and eyes. They pass out through a glass stopper. The whole of the micrometer screw, including the head and counting device, is now enclosed in the evacuated glass apparatus, thus eliminating the mercury column RQ₃. The screw is driven by means of a right-angled bevelled gear, which is turned by a ground glass stopper. The fractions of turns are read off on the micrometer head through the glass, and the whole turns on a cyclometer, also enclosed.

A good deal of attention was paid to the measurement of the magnetic field H. In the former experiments this was done by the change of resistance of a bismuth spiral. This method is not a very accurate one with magnetic fields of the strength used, and could not be employed when the measurements of e/m were actually being carried out. This introduces the chance of a further error, owing to possible changes in the temperature of the magnet, if, as was the case, the exciting current is used as an intermediate indicator of the magnetic field. The procedure adopted in these

* Cf. 'Phil. Mag.,' 1913, vol. 26, p. 452.

experiments was more complicated but more reliable. A marble block of square cross-section was wound with 20 turns of fine wire, so that all the induction was along the axis of the solenoid and was calculable. The terminal wires were carried back to the middle of the coil, so as to cancel the sideways induction, and then twisted together. This standard of induction was placed with its axis parallel to the magnetic field in the place between the poles of the electromagnet occupied by the paths of the moving ions in the measurements of e/m .

The cross-section of the solenoid was 1.407 cm.^2 , so that the area of the field was comparable in the two cases. The solenoid was arranged in series with a sensitive fluxmeter, and the throw measured when the electromagnet was reversed. The fluxmeter was then placed in series with the secondary of a standard mutual inductance which was tested at the Bureau of Standards and found to be equal to 0.010175 henry. The throw of the fluxmeter was then determined, when a known current in the primary of the mutual inductance was reversed. This current was measured by comparing the fall of the potential, when it flowed through a Wolff standard resistance, with the electromotive force of a cadmium cell, which had been tested by Hulett, using a Wolff potentiometer. As a matter of fact the current in the primary was adjusted so that the current it induced would produce the same calculated throw in the fluxmeter as would be produced by a field of 3000 lines threading the standard marble inductance. The current exciting the magnet was then adjusted until the two throws, due to reversal, were exactly equal. In this way errors arising from the varying sensitiveness of different parts of the fluxmeter scale were eliminated. Before testing the effect of the magnet several preliminary reversals were carried out to get rid of effects due to hysteresis.

In this way the measurement of the magnetic field was made to depend upon a knowledge of the following quantities:—The calculated inductance of the solenoid, the standard of mutual inductance, the standard of resistance, and the electromotive force of the cadmium cell. These are all known with a high degree of precision, so that the limit of accuracy would appear to be set by the accuracy with which two equal deflections of the fluxmeter can be compared. The deflections were about 300 scale divisions, and an accuracy of 0.5 per cent. is probably a conservative estimate of what was attained. An attempt was made to reduce the comparison to a null method, but this was unsatisfactory on account of the difference in the time constants of the circuits compared. The insertion of such self inductances as were available did not mend matters very much, so that the adjustment to equality of deflections was adopted.

So far the above process is open to one of the objections to the bismuth spiral method, since it can be used only when the measurements of e/m are not being carried out. This difficulty was overcome by using as an intermediate standard a single circular turn of wire attached to the end of one of the pole pieces. The flux through this was checked up against that through the solenoid by means of the fluxmeter, and the throw from the single turn due to reversing the magnet could be compared with that from the mutual inductance at any time when the measurements of e/m were being made. As a matter of practice it was found that if the temperature of the magnet was kept constant the magnetic field due to a given exciting current remained the same, so that to keep the same magnetic field it was only necessary to watch the temperature of the magnet and the value of the exciting current as shown on a standard Weston ammeter. Separate tests showed that the flux across a square centimetre did not vary as much as 1 per cent. over the whole area of the flat ends of the pole pieces (40.7 sq. cm.). The magnetic fields used were thus very uniform.

The static potential difference between the strip and the opposite plates was always kept at exactly 200 volts. This was done by means of a battery giving rather over 200 volts in series with a variable opposing potential taken from a few cells in series by means of a sliding rheostat. The potential was adjusted to 200 volts by the potentiometer; 1,001,000 ohms was placed across the whole battery, and the drop on the 1000 ohms was compared with a standard electromotive force.

The measurements of e/m were made by a slight modification of the balancing method* described in one of my former papers.† This type of method has the great advantage that the immediate determination of e/m requires only two simple measurements which can be carried out in about a minute, so that the change of e/m with time can be followed even when it is altering rather rapidly. I have compared this method with the more laborious slit method under the improved conditions, and they agree absolutely, so far as I am able to tell. It is probable that the deviation from the theoretical formula observed in the older experiments† was due either to the theoretical conditions not having been satisfied or to an inaccurate knowledge of some of the data.

In the former measurements the value of e/m for the negative electrons was taken as a kind of absolute standard in determining e/m for the positive ions. This method possessed certain advantages when it was important to determine with some degree of reliability even approximate absolute values

* See also 'Phil. Mag.,' 1913, vol. 26, p. 452.

† 'Phil. Mag.,' 1908, vol. 16, p. 740.

of e/m for the positive ions, but it cannot claim to be of value in determining the value of e/m for the positive ions with precision in the present stage of development of this method of experimenting. In fact the accuracy which has been attained in the measurement of e/m for the positive ions in this way is, so far, very much greater than that for the negative electrons. Very likely this is to a large extent simply a matter of insufficient experience, but there are difficulties, such as those conditioned by electron reflection, that arise in the case of the negative electrons which do not occur with the positive ions. At any rate, the measurements that were made with the negative electrons in the former apparatus led to quite irregular results, so that no use has been made of them in the present investigation. It is, however, desirable to have some check on the results which does not depend directly on the rather considerable number of measurements required in getting absolute values. This was furnished by placing potassium sulphate on the strips and measuring e/m for the positive ions from this substance. The writer has already shown that the positive ions from the salts of the alkali metals are univalent atoms of the constituent metal. The ions from potassium sulphate have a value of e/m which is indistinguishable from that of the majority of the ions given by the metals tested, so that this substance is extremely well adapted for checking the values otherwise obtained.

It is worth while pointing out that in the old experiments in which the value of e/m for the electrons is made use of, the results are over-corrected in any event, as the value e/m (1.88×10^7) which was taken as the standard is about 6 per cent. higher than that which is now accepted. Moreover, the correction for the lack of uniformity of the electrostatic field which is discussed in the 'Philosophical Magazine,' 1908, vol. 16, p. 763, must now be very small, as the clearance between the strip and the surrounding plate (0.01 cm.) was only about one-tenth of the width of the strip. It is rather significant that the values of e/m do tend to run about 2 per cent. lower than what seems to the writer to be the most probable value.

Results of the Experiments.

The substances which have been tested with the improved apparatus and method are platinum, potassium sulphate, manganin and iron. The number of different kinds of metal strips which can be subjected to a sufficiently extensive examination in this way is rather limited, as there are not many which will stand the required tension at high temperatures. The strips were carefully cleaned before mounting. The part which was subsequently heated was never touched except with platinum tweezers, and the greatest care was taken to avoid any possible contamination of this part of the

strip with possible impurities. The heating current was regulated so that the thermionic current was kept at a suitable value to make measurements with. This involved a gradual increase in the temperature of the strip as the heating progressed, on account of the decay of the emission with time. The pressure of the external gas was less than 0.001 mm. on the McLeod gauge, except in certain special experiments. The temperature of the strip was obtained from its resistance, although it is only a matter of secondary importance.

The results obtained are expressed in terms of the electric atomic weight m/m_1 of the ions, which are supposed to be univalent, instead of e/m . The values of m/m_1 are obtained by dividing the value of e/m for a univalent electrolytic ion of unit atomic weight, which is 9649 E.M.U., by the measured values of e/m . This enables a direct comparison with the chemical atomic weights (in terms of $O = 16$) to be effected. The values of e/m were obtained by substituting the experimental numbers in the formula

$$e/m = \frac{9}{2} \frac{Vx^2}{H^2z^4},$$

where V is the electrostatic potential difference between the opposite plates, H is the intensity of the magnetic field, x is half the displacement of the balance which occurs when the field is reversed, and z is the distance between the front of the strip and the front of the opposite plates. V was always 2×10^{10} E.M.U., and H was always 3000 E.M.U., $2x$ was comparable with 0.5 cm., and z with 1.35 cm.

As an illustration of the uniformity of the results given by this method under favourable conditions the numbers given by one of the preliminary tests may be cited. A strip which was clean in appearance, but which had not been specially cleaned, was heated for several hours and then kept under fairly continuous observation for a period of five hours longer.

During this time 16 determinations of m/m_1 were made and all of them lay between 39.75 and 40.2. In general the uniformity is not so high as this, although deviations in excess of 3 per cent. of m/m_1 are very rare. A good deal seems to depend on whether the strip is comfortable or not. A minute twisting or displacement of the strip in between two readings will cause a serious deviation. The position of the balance can easily be determined to one-hundredth of a turn (0.000635 cm.). This means about 0.1 per cent. of $2x$.

Another preliminary test gave the following values of m/m_1 . The length of time the strip had been heated and the instantaneous platinum resistance temperatures are also given.

Time (minutes) ...	0	10	15	25	30	35	45	55	70	85
Temp. (° Pt)	468	468	468	492	492	492	492	492	503	503
m/m_1	40·6	40·7	40·8	40·2	40·4	40·7	40·6	40·6	40·1	40·3
Time (minutes) ...	100	105	125	150	170	190	195	205	210	285
Temp. (° Pt)	525	525	525	525	525	535	535	535	535	668
m/m_1	39·9	39·9	39·8	39·9	39·8	39·8	39·3	40·1	39·1	39·9
Time (minutes) ...	300	310	320	330	345	350*	360	370	380	385
Temp. (° Pt)	668	668	668	690	690	690*	480	514	514	525
m/m_1	39·3	39·5	39·8	39·8	39·9	40·6*	39·7	39·7	42·9	41·1
Time (minutes) ...	390	395	480	520						
Temp. (° Pt)	525	525	579	614						
m/m_1	41·6	41·0	40·4	39·6						

The strip broke at this stage. At the point indicated thus* it was found to be behaving unsatisfactorily. The strip was cooled and the apparatus taken down, when it was found that the strip had warped and come into contact with one side of the slit in the brass plate. The subsequent measurements were taken after the strip had been readjusted and the apparatus set up again.

It is clear that there is no definite indication of any change in the electric atomic weight of the ions given off by the above strip in the space of 8 hours 40 minutes during which it was heated. The mean value of the electric atomic weight is very close to 40. The breaking of the strip is to be attributed to the combined effect of the tension of the spring and the high temperature. The resistance of the strip only gives the average temperature, and no doubt the central portions were much hotter than the recorded temperatures indicate.

In order to find out if long continued heating would change the nature of the ions another carefully cleaned strip was taken and heated for 36 hours under + 200 volts, but without any tension. This was accomplished by means of the limiting screw already referred to. The screw was then turned back so that the spring would pull the hot strip taut. Three measurements extending over 25 minutes were then made before the strip broke. They gave the following values of m/m_1 in succession: 25·1, 25·3, 24·2. Thus after the positive ionisation from platinum has been allowed to decay for a long time it is found that the ions have a much smaller atomic weight than those which are first emitted.

After some experimenting it was found possible so to adjust the tension of the spring that not only both the stages referred to but also indications of a third kind of ions could be demonstrated on the same strip. Some of the values given by the most satisfactory experiment of this kind are indicated thus: \times , in fig. 1. Some of the numbers in the table above are also plotted thus: \blacktriangleleft for comparison. The figure also contains some of the

data given by a test made on potassium sulphate. In this experiment a strip was glowd out until it had lost the power of emitting positive ions except at a very high temperature, and then a small quantity of a solution

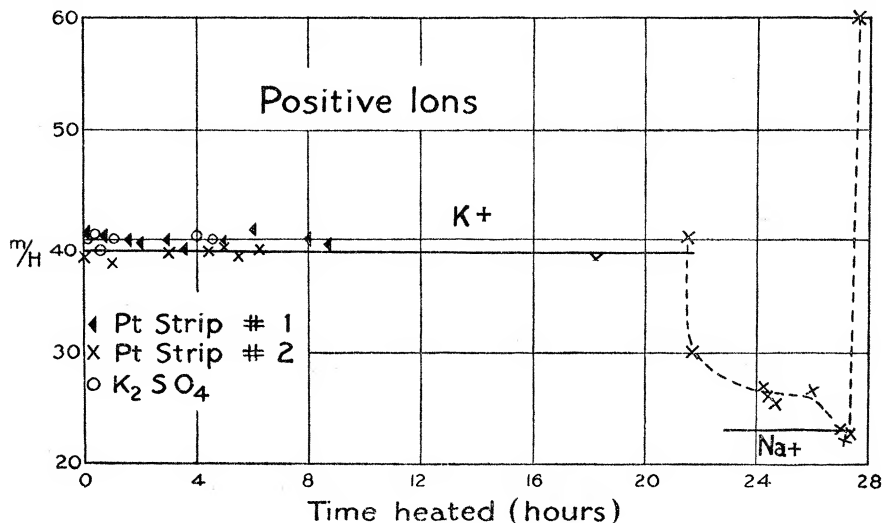


FIG. 1.

of pure potassium sulphate in distilled water was placed on it. In making the measurements the strip was stretched by the spring as in the other cases. In fact the clean platinum strip was glowd out until the emission at 1011° Pt was too small to make measurements with. When the strip was cold the apparatus was taken down and the solution of K_2SO_4 sprayed on to it in such a manner that none of the spray got on to any part of the apparatus except the front surface of the strip. It was then found that the emission at 320° Pt was plenty large enough to work with. All the measurements which were made in this experiment are collected in the following table:—

Time heated (minutes)	0	10	17	25	30	40	50	60	235	275	280
Temperature	320	320	330	330	330	330	330	350	350	500	500
m/m_1	40.4	40.6	41.1	40.7	39.2	39.7	40.1	40.2	40.3	41.6	39.8
Mean = 40.2.											

Only a few of these values of m/m_1 for the ions from potassium sulphate are plotted in the figure. They are indicated thus: \circ . The current which was flowing from the hot strip during the experiments recorded in this paper was not maintained constant. It was, however, kept at a value which was convenient to work with, and was thus always comparable with 0.01 electrostatic unit.

Returning to fig. 1 the horizontal line on the left represents the chemical
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value of m/m_1 for the monovalent ion K_+ , and the horizontal line to the right the corresponding value for Na_+ . The points marked thus: \times , do not represent the whole history of the ions from strip No. 2. This strip was heated for about 14 hours before commencing observations, in order to drive off most of the initial ionisation. Numerous independent experiments have amply shown that this initial ionisation is made up entirely of ions for which m/m_1 is equal to about 40, so that we may conclude that during the first 36 hours of heating under these conditions practically all of the positive ions emitted are of the same character. Although the experimental value of m/m_1 for them runs a little higher than the chemical value for K_+ , there is no demonstrable difference in the numbers given by them and those given by the ions from K_2SO_4 . As there are good reasons for believing the latter to be atoms of potassium which have lost an electron, there does not, so far, seem to be any reason for doubting the identity of the ions in the two cases. Alternative possibilities will be considered later.

Although the data are not at all precise, it is worth while to estimate the amount of matter which is emitted in the form of these positive ions. In the above experiment in which the strip was under observation until all the ions for which m/m_1 is in the neighbourhood of 40 had been emitted, the current during the 14 hours of preliminary heating was greater than afterwards. Allowing a factor of about 2.5 for this, I find that the total quantity of electricity carried away in the form of these ions would be 10^{-6} coulomb or 10^{-7} E.M.U. Putting $e/m = 246.5$ (the value for K_+) the mass of matter carried away in this form $= 4.05 \times 10^{-10}$ gram. If an equal amount escapes from the back of the strip the total would be 8.1×10^{-10} gram. The mass of the heated part of the strip was approximately 5.5×10^{-2} gram. Thus the proportion of the matter present which is emitted in the form of these positive ions is about 1.5×10^{-8} , or 1.5×10^{-6} per cent. Some data given by Horton* for an experiment made at a much higher average temperature (1190° C.) lead to a rather similar estimate. The similarity of these two estimates rather points to the view that the quantity of electricity emitted in the form of these ions does not depend much on the temperature of emission. The simplest explanation of this result would be that practically all of the available matter is expelled in the ionised form. If that is the case the total amount of matter concerned is so small that its detection by chemical methods is not very hopeful. This question cannot be regarded as definitely settled by the data now available, as the dependence of the total amount of matter emitted in the form of a given kind of ions upon the method of heating requires further examination.

* 'Roy. Soc. Proc.,' 1913, A, vol. 88, p. 135.

Turning again to fig. 1 we see that after about 36 hours of heating (22 on the diagram) there is a rather sharp drop in the value of m/m_1 , after which values in the neighbourhood of Na_+ are approached somewhat gradually. In this region the values obtained are apt to be irregular and point to the occurrence of a mixture of ions. It may be that the values in the neighbourhood of 26 correspond to something definite, but the irregularity of the results usually obtained when the average value is in this neighbourhood do not lend support to such a view. Until further evidence appears it seems most reasonable to suppose that in this neighbourhood we are dealing with a mixture of Na_+ and K_+ . With platinum strips the sodium values only occur at a high temperature and after continued heating. They never last very long, so far as I have been able to observe.

With the strip under consideration the last value, which was obtained very shortly before the strip broke, is very close to 60. With very old strips I have frequently observed the presence of ions for which m/m_1 lies between 50 and 60. I am inclined to attribute them to the presence of Fe_+ (56). Unfortunately they do not last very long, and the behaviour at this stage is rather irregular, so that it has not been possible to get really accurate results. I have often looked for heavy ions such as Pt_+ ($m/m_1 = 195$) from strips which have been subjected to long continued heating, but I have never been able to observe anything of the kind.

After making several unsuccessful attempts with gold strips, which always broke under the tension required to keep them straight, before a sufficiently large or permanent ionisation to make measurements with could be obtained, strips of manganin were tried. These were rolled from resistance wire to the requisite width and thinness, and were cleaned in ether, dilute nitric acid, and distilled water before being mounted. The initial heating current was 0.65 ampère, and this had to be raised gradually to 0.84 ampère as the heating progressed, owing to the decay of the emission. No attempt was made to estimate the temperature, but it was not very different from that of platinum when heated for the same length of time. A series of measurements of m/m_1 which were extended fairly evenly over a period of four hours gave the following successive numbers:—39.3, 39.7, 39.4, 41.0, 40.2, 39.3, 39.7, 39.5, 39.7, 40.0, 41.4, 40.8, 40.0; mean 40.0. Thus the positive ions given off by manganin have the same electric atomic weight as the bulk of those given off by platinum, and there seems to be no valid reason against referring them to the same ingredient.

Two different specimens of iron wire were tested in the same way. Both of them were said to be especially pure iron, but they were not analysed. The wires were rolled into strip and washed with ether, dilute

hydrochloric acid, and distilled water, before mounting. The specimen from the first sample had a resistance of 174 arbitrary units at 40° C. Only four observations were made on this specimen. The times, resistances, and values of m/m_1 were as follows :—

Time heated (minutes)	10	25	46	55	
Resistance (arbitrary units) ...	524	524	504	504	
m/m_1	39·9	39·9	39·8	40·0	Mean = 39·9.

Two specimens from the second sample were tested. The first gave the following numbers :—

Time heated (minutes) ...	0	?	39	?	?	75	80	95	105
m/m_1	24·2	37·1	37·8	33·3	39·9	42·6	40·7	46·0	73·5

Thus the first specimen gave no indication of anything except the ions which have been attributed to potassium, and the second gave rather similar values over most of the corresponding time. In addition, the second specimen gave indications of something with a lower value of m/m_1 , which, may have been Na₊ (23·05) at first, and also considerably higher values, 46 and 73·5, just before the strip broke. These are well above the potassium value, and may be taken to indicate Fe₊ (56). The last high value is a little uncertain, as the strip broke before the observation could be repeated, but there is no doubt that values much higher than 40 were being got at this stage. Another specimen from this second sample was tested. Unfortunately, both the initial and final stages were missed owing to the occurrence of accidents. The results, however, are of interest, as confirming the conclusion drawn from the other tests, that the bulk of the ions from iron have the same value of m/m_1 as those from platinum and manganin. The data given by this specimen are as follows :—

Time observed (minutes)	0	10	30	60	90	180	195	215	225	255	315
Resistance (arbitrary units)...	1084	1084	1144	1244	1314	1594	1594	1614	1694	1804	1894
m/m_1	38·3	39·5	40·0	40·0	39·9	42·1	40·5	40·5	39·7	39·4	40·9
Mean m/m_1 = 40·1.											

The resistance at 40° C. was 334 in the same units.

I have already mentioned that the view that the positive ions from freshly heated metals consist of charged atoms or molecules of one or more of the commoner gases, such as carbon monoxide, hydrogen, carbon dioxide, nitrogen or oxygen, has obtained a considerable number of adherents. As the respective electric molecular weights of the ions which might be expected to arise from these gases are the following: CO₊ = 28, H₊ = 1, H₂₊ = 2, CO₂₊ = 44, N₊ = 14, N₂₊ = 28, O₊ = 16, and O₂₊ = 32, it will probably be conceded that the present experiments do not lend any support to such a view. The only common gas for which the value of m/m_1

is near enough to the measured values is argon ($\text{Ar}_+ = 39.9$). The value for argon would, in fact, fit the experimental results better than that for potassium, but there are other reasons, which will be considered below, which seem to the writer to make potassium the more probable constituent. It would, of course, be a matter of very great interest if it could be established that these ions are charged atoms of argon.

Let us review very briefly some of the more important experimental results which tend to support the view that these ions are charged atoms or molecules of one or more of the commoner gases. Most of these will be found enumerated in the following list:—

(1) A platinum wire, which has lost the power of emitting positive ions owing to continued heating in a vacuum, is found to regain this property to a considerable extent if it is re-heated (*a*) in air at atmospheric pressure, and especially (*b*) if it is heated in a bunsen flame.*

(2) A similar recovery takes place when the wires are exposed to various gases under a pressure of 50 to 100 atmospheres at a relatively low temperature† (about 200°C).

(3) When most metals are heated there is a considerable evolution of gas, the bulk of which usually consists of hydrogen, carbon monoxide, and nitrogen.

(4) When a wire has been heated for a long time so that the emission in a vacuum has become too small to measure, there is an emission in different gases, which seems to be a definite function of the nature and pressure of the gas. This phenomenon has been most completely studied in the case of platinum in an atmosphere of oxygen.‡ The facts have been explained by the writer on the hypothesis that the metal absorbs or adsorbs the gas, which it re-emits in the form of charged atoms. It has been suggested by various writers that the initial emission is an intensification of this phenomenon, owing to the presence of much larger amounts of absorbed gas in the original metal.

(5) Horton§ has found that carbon monoxide has a greater power of stimulating the emission of positive ions both from hot platinum and from heated salts than the other common gases, with the exception of hydrogen.

(6) Determinations by Garrett|| of e/m for the positive ions given out by aluminium phosphate when heated led him to conclude that these were atoms of hydrogen.

* Cf. Horton, 'Roy. Soc. Proc.,' 1912, A, vol. 88, p. 131.

† Z. Klemensiewicz, 'Ann. der Phys.,' 1911, vol. 36, p. 796.

‡ O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 1.

§ Horton, 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, p. 89.

|| Garrett, 'Phil. Mag.,' 1910, VI, vol. 20, p. 582.

We shall now consider how the facts just enumerated can be reconciled with the results of the measurements of m/m_1 which have been described. In the absence of definite information, the obvious explanation of (1) (a) and (1) (b) seemed to be that the revived ionisation was due to a different cause from the ionisation from the fresh wire; that the initial ionisation might be due to the impurities in the wires, which have been tentatively attributed to potassium, whereas the revived effect might be due to the re-emission of absorbed gas, air in the case of (a), and gases from the bunsen flame in the case of (b). This view can readily be subjected to the test of experiment, for, if it is correct, the ions from the revived wire should have a value of m/m_1 different from that of those from the fresh wire. The tests were carried out with the platinum strips, and the effect of heating in dry filtered air at atmospheric pressure was tried first. The strip was glowed out until there was no measurable emission at about 700° Pt. It was then heated in air in the apparatus with the strip loose. This heating was carried out during a succession of short intervals with longer cold intervals between, the object being to prevent the whole apparatus from getting heated. After the strip had been heated in air at a high temperature for about 10 minutes altogether, the apparatus was taken down, the strip tightened up, and the distance z measured. The subsequent observations are collected in the following table:—

Time heated (minutes)	0	25	30	37	50	85	115	125	135	145	160
Temperature (° Pt) ...	396	430	430	445	445	445	450	589	611	667	700
m/m_1	37·9	38·4	38·8	38·7	39·1	38·8	39·5	39·3	39·8	39·4	38·8
Mean $m/m_1 = 39·0$.											

The above values run about 2·5 per cent. lower than those given by a fresh strip. This may mean that there is a small admixture of lighter ions which are charged atoms or molecules of gas absorbed from the air. This does not seem very likely, however, as the value is very near that given by strip No. 2 shown in fig. 1 which had been heated to about the same stage before commencing observations. It seems more reasonable to conclude that the lower values are due to a slight admixture of the ions for which m/m_1 is near the sodium value, which are apt to be present in sufficient quantity to exert some influence at this stage. It is quite clear, at any rate, that the bulk of the ions after reviving the wire by heating in air have the same value of m/m_1 as those emitted by a fresh wire.

Another platinum strip was then taken and treated somewhat similarly, except that instead of heating in air at atmospheric pressure it was taken down and heated in a bunsen flame for a few minutes. It was then found to give a large positive emission at a much lower temperature than

before. The numbers given by this experiment are shown in the following table:—

Time heated <i>in vacuo</i> (minutes)	5	10	20	30	35	40	60	105	120	130	133
Temperature (° Pt) ...	405	405	427	473	473	473	495	506	518	541	541
m/m_1	40·2	40·1	40·2	39·0	40·7	39·6	40·6	39·6	39·9	40·2	40·0
Mean $m/m_1 = 40·0$.											

This experiment shows that the large ionisation which is obtained when a glowed out platinum wire is heated in a bunsen flame consists of ions for which the value of m/m_1 is the same as for the ions from a freshly heated wire. This conclusion was confirmed by a repetition of the experiment but there does not seem to be any point in quoting the data which were obtained.

Two views suggest themselves as to the material origin of the ions observed in these experiments. Either the material is present in the metal all the time, to a considerable extent even after continued glowing in a vacuum, but is so securely held that it is unable to diffuse to the surface and produce ionisation. In that case the effect of heating in different gases may be imagined as resulting in a loosening up of the structure of the material by the diffusion of the gases into the interior. In this way a means would be provided for the diffusion of the ionisable material to the surface of the metal. On the other hand it is possible that the ionisable material is actually formed by the action of the gases on the heated platinum. This would involve the rather radical supposition that the atoms of the metal were being broken up by the actions occurring. I think the balance of evidence at present available is against such a view. Many years ago* I made experiments to see if a platinum wire which had lost the power of positive emission would recover it if it was allowed to remain standing in a vacuum. I only obtained small and uncertain effects. Of course, this does not prove that such actions may not occur with facility at higher temperatures. But the experimental results at present available indicate that the bulk of the positive ions given by different elements have an electric atomic weight of about 40. When one considers that this is true of the element carbon, whose atomic weight is 12, it points rather to the presence of a common impurity than to the occurrence of atomic disintegration. Moreover the following experiment shows that merely straining the metal will cause a revival of the positive emission. This, I think, supports the idea that the renewal of the emission under various circumstances is mainly a mechanical effect. I do not wish to indicate that I believe the question under discussion to be settled beyond the possibility of doubt, but I believe the balance of evidence at present available favours some such view as that just indicated.

* 'Comptes Rendus Congrès de Radiologie,' Brussels, 1905.

The experiment referred to was made with the manganin strip, which gave a mean value of $m/m_1 = 40.0$. After it had been heated for some time it gave an emission of 15 divisions in 30 seconds at a certain temperature. Without altering the heating current or letting down the vacuum it was found to be possible so to rotate the apparatus that the strip became inclined at 35° to the magnetic field instead of parallel to it. With the rather large heating current (0.75 ampère) which the strip was carrying, there is then a considerable pull on it due to the magnetic field. The magnetic field was rapidly reversed a number of times to get as large an effect as possible, and the emission when measured at the original temperature, which was considerably higher than that at which the straining was carried out, was found to be 308 divisions in 30 seconds. It had thus increased by a factor of more than 20. The value of m/m_1 for the ions which carried this increased emission was then measured and found to be 39.4, which agrees with the previous value within the limits of experimental error. The result of this experiment rather indicates that the revival under pressure observed by Klemensiewicz (2) may be due to the mechanical action of the pressure directly, although there are many other causes which may have played a part in an experiment of that character.

I shall now consider the remaining reasons (3) to (6) for believing in the gaseous origin of these positive ions rather more briefly. In regard to (3) I* at one time examined the emission of gas from a fresh platinum wire rather carefully and compared it with the simultaneous emission of positive ions. Apart from the fact that both emissions were largest at first and decayed with time there was no simple relation between them. C. J. Davisson† has also recently shown that there is no relation between the emission of gases by salts and the emission of positive ions from them.

As regards the greater efficiency of carbon monoxide and hydrogen (5) it is well known that both these gases have an exceptional capacity for diffusing into various metallic solids, and they would therefore be exceptionally effective, in loosening up the pores of the metal. In addition, they are both reducing agents; and reduction has been found to facilitate the emission of positive ions in the case of some salts.‡

So far as (6) is concerned, I myself have never been able to detect the existence of positive ions, either from fresh metals or from salts when heated in a vacuum, which have values of m/m_1 anywhere near so low as that for

* 'Comptes Rendus Congrès de Radiologie,' Brussels, 1905.

† C. J. Davisson, 'Phil. Mag.,' 1912, vol. 23, p. 139.

‡ O. W. Richardson, 'Phil. Mag.,' 1911, vol. 22, p. 698.

H_+ or for H_{2+} . This result has been confirmed by Davisson.* It seems fairly certain that with ordinary specimens of aluminium phosphate and with metals the proportion of hydrogen ions, even if there are any at all, must be much smaller than the 10 per cent. found by Garrett. This does not preclude the possibility that when a large amount of hydrogen is allowed to diffuse from the interior of an old platinum tube into air at atmospheric pressure there is a current which is carried by charged atoms of hydrogen. I† once concluded that this was the case; but the inference was an indirect one, and until the electric atomic weight of the carriers has been determined under these conditions one has to bear in mind the possibility that the diffusing hydrogen simply washes some heavier ionisable constituent out of the hot metal.

Turning to (4), I have made several attempts to settle, by direct measurement of m/m_1 , the nature of the positive ions which are emitted when an old wire is heated in air or oxygen. The method has been to glow out a strip until the emission was very small and then to measure m/m_1 for the ions which make up the measured emission when air or oxygen at a low pressure is let into the apparatus. So far it has not been possible to get enough current to make measurements with at a low enough pressure for the method to be applicable. I do not regard this problem as insuperable, but it happens that the proper conditions have not yet been realised. In the absence of direct evidence as to the nature of these ions it would appear illegitimate to infer from their assumed nature that of other ions which are produced under different conditions.

So far the reasons which make me think the ions whose measured electric atomic weight is very close to 40 are most likely to be K_+ have hardly been considered. As a matter of fact the mean of the best values is very close to 40.0, so that either $Ar_+ = 39.9$ or $Ca_+ = 40.07$ would fit better than $K_+ = 39.1$. Moreover, I am informed by manufacturers of platinum that potassium is not an impurity which one would expect to find in this metal; whereas calcium might be looked for, as the metal is heated at one stage in lime crucibles. On the other hand, any slight lack of uniformity in the electrostatic field due to the gap between the strip and the surrounding plate tends to make the measured value of m/m_1 too high. What is perhaps more convincing is the fact that the positive ions from potassium sulphate itself also gave values of m/m_1 which were too high and which agreed very well with those given initially by the hot metals. There are very good reasons for believing that the positive ions from potassium sulphate are K_+ . The

* C. J. Davisson, *ibid.*, p. 147.

† O. W. Richardson, 'Phil. Trans.,' 1906, A, vol. 207, p. 54.

electric atomic weight of the ions from Li_2SO_4 , Na_2SO_4 , K_2SO_4 , Rb_2SO_4 , and Cs_2SO_4 , after these salts have been heated for some time,* correspond respectively to Li_+ , Na_+ , K_+ , Rb_+ and Cs_+ . Moreover, on first heating Li_2SO_4 , Na_2SO_4 , and many other salts, the positive ions given off have a value of m/m_1 which corresponds to K_+ . This shows that potassium is relatively the most efficient of the commoner alkali metals in emitting positive ions. It is a very widely distributed element, and its very marked capacity for ionisation would lead one to expect that it might give rise to the bulk of the ions emitted by the metals if the ions arise from adventitious impurities. The objection to calcium is that its efficiency does not appear to be comparable with potassium in this respect, and one would not expect Ca_+ to come off prior to Na_+ , as is observed in the case of platinum. It is true that iron was found to be an exception in this respect, but the initial presence of sodium was only recorded once. This shows that at any rate there was only a small amount, which may have been caused by accidental superficial contamination. The emission of $m/m_1 = 40$ in large excess, and long before there was any considerable amount of $m/m_1 = 23$, in the case of platinum, has been amply verified in numerous experiments. In any event it is doubtful whether much attention should be paid to chemical evidence, as the amounts of matter required are extremely small in all cases. There does not, at present, seem to be any evidence other than the value of m/m_1 , which would tend to support the view that these ions are charged atoms of argon, and the same may be urged against the hypothesis of heavier atoms provided with multiple charges.

In conclusion I wish to thank my former assistant, Mr. E. S. Taylerson, to whose ingenuity and manipulative skill the measure of success attained by this investigation is largely attributable.

* O. W. Richardson, 'Phil. Mag.', 1910, vol. 20, p. 981.
